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ELECLTROCHEMICAL REDUCTION OF p-ACETAMIDOBENZENE SULPHONYL CHLORIDE

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The study of the electrochemical reduction of p-acetamidobenzene sulphonyl chloride under galvanostatic conditions show that the hydrolysis of both the acetamido group and sulphonyl chloride group enhanced when the temperature is maintained above 303 K and the *p*H of the electrolyte is less than 7.0. The results obtained while using different supporting electrolytes are presented. The cyclic voltammetric studies show that the reduction of p-acetamidobenzene sulphonyl chloride proceeds through sulphinic acid formation.

Keywords: Sulphonyl chloride, sulphinic acid, hydrolysis

INTRODUCTION

The chemical and the electrochemical reduction of simple and substituted benzene sulphonyl chloride results in the formation of useful products such as benzene sulphinic acid, sulphones and thiophenols, which are extensively used in pharmaceutical and dye industries. A study of the electrochemical reduction of aromatic sulphonyl chloride specifically p-acetamidobenzene sulphonyl chloride (ABSC) was undertaken to assess the potential of such a process as an alternative to the chemical method of reduction of ABSC by using zinc as the reducing agent. Zinc being relatively expensive as well as the zinc ions let out in the effluent causing heavy metal poisoning an electrochemical route may be preferable.

The present study was directed towards devising an efficient electrochemical process for the reduction of ABSC, using solid electrodes like copper, lead and zinc deposited copper electrode.

EXPERIMENTAL

Cyclic voltammetry studies were carried out using the cell and equipments described elsewhere [1] for the reduction of p- acetamidobenzene sulphonyl chloride and for its reduction intermediate namely p-acetamidobenzene sulphinic acid. Preparative scale experiments were carried out under galvanostatic condition. Ceramic porus pot was used as the separator to prevent the oxidation of the starting material and the product at the anode surface. Later on cation exchange membrane was used as the separator in order to prevent the migration of chloride ion and subsequent discharge of chlorine which were observed while using ceramic porous pot. The addition of the depolariser was only in instalments in order to maintain an approximately constant reactant concentration throughout the course of electrolysis.

RESULTS AND DISCUSSION

Voltammetric studies

A typical cyclic voltammogram of ABSC (3×10^{-2} *M*) in ethanolic hydrochloric acid (1 *M*) on glassy carbon electrode is given in Fig. 1. The voltammogram shows two well defined well separated cathodic peaks. In the return sweep no anodic current is observed. The peak currents (I_p) for both waves linearly increase with the square root of the sweep rate ($\nu^{1/2}$) giving rise to a constant value for $I_p/\nu^{1/2}$. The peak potentials of both waves also get shifted to cathodic region with the increase of sweep rate. The $E_p - E_{p/2}$ value is quite high and this value also increases with increasing sweep rate.

While studying the effect of concentration on peak current and peak potential it is observed that there is a linear increase of peak current with increasing concentration of ABSC at a constant sweep rate. The peak potentials of both the waves also get shifted to negative side while the concentration is increased. This type of behaviour should correspond to a

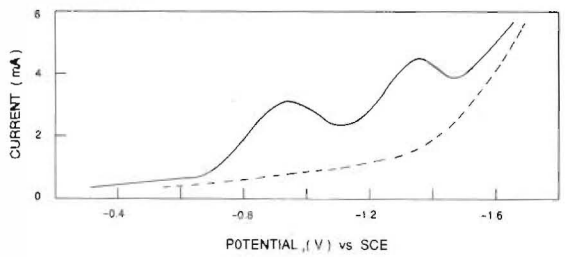

Fig. 1: Cyclic voltammograms of p-acetamidobenzene sulphonyl chloride (3 x 10^{-2} M) in ethanolic HCl on glassy carbon electrode

simple irreversible electron transfer or to a reversible electron transfer followed by an irreversible chemical reaction.

Fig. 2 shows the cyclic voltammogram obtained for the reduction of p-acetamidobenzene sulphinic acid which is considered to be a reduction intermediate product of ABSC. The experimental conditions and the sweep rate for the cyclic voltammetry study of p-acetamidobenzene sulphinic acid are maintained very similar to the conditions and sweep rate maintained for the cyclic voltammetric study of ABSC.

A well defined diffusion controlled single wave is obtained whose peak potential, coincides with that of the second wave obtained in the case of ABSC and also the effect of sweep rate and effect of concentration on the peak current. Peak potential and $E_p - E_{p/2}$ are very similar to the second wave. This confirms that during the course of first wave for ABSC, sulphonyl chloride group gets reduced to first wave for ABSC, sulphonyl chloride group gets reduced to sulphinic acid group involving two electrons in the reduction process when comparing the peak current of the first wave (Fig. 1) with that of the single wave (Fig. 2) one can come to the conclusion that only two electrons are involved in the further reduction of sulphinic acid leading to the formation of sulphone. Sulphone is also an electroactive material and can undergo further reduction leading to the formation of thiophenol. This reduction may be taking place at hydrogen evolution potential and the current due to this reduction process may get merged with hydrogen evolution current. So one can accept the following reaction scheme proposed for other simple and substituted benzene sulphonyl chloride [2-7].

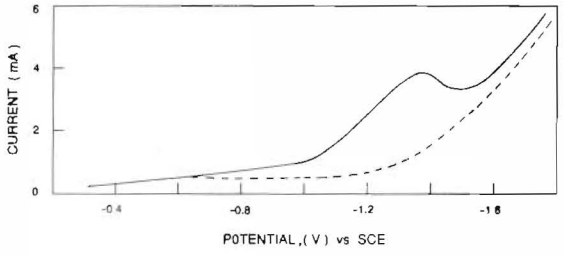

Fig. 2: Cyclic voltammograms of p-acetamidobenzene sulphonyl chloride (3 x 10^{-2} M) in ethanolic HCl on glassy carbon electrode

Reaction scheme

$$2RSO_2Cl + 4H^+ + 4e \longrightarrow 2RSO_2H + 2HCl$$

$$2RSO_2H + 2H^+ + 2e \longrightarrow RsO_2SR + 2H_2O$$

$$RSO_2SR + 4H^+ + 4e \longrightarrow RSSR$$

$$RSSR + 2H^+ + 2e \longrightarrow RSH$$

$$\mathbf{RSO_2Cl + 6H^+ + 6e \longrightarrow RSH}$$

Preparative scale electrolysis

Reductions were carried out under different temperatures and current densities using alcoholic HCl, alcoholic H_2SO_4, aqueous acids and aqueous sodium chloride with and without zinc as mediator, as electrolyte. Since both the acetamido group and sulphonyl group are easily hydrolysable, the temperature, *p*H and electrolyte composition play a major role in enhancing or suppressing the rate of hydrolysis. Once the hydrolysis of sulphonyl group to sulphonic acid takes place the reduction will not at all take place because the reduction of sulphonic acid is not possible. Even though the electrolytic conditions are fixed to suppress the rate of hydrolysis, some amount of sulphonic acid is formed as a result of hydrolysis. The product analysis shows that during the electrochemical reduction of ABSC, mixture the following products are identified.

1. p-acetamido benzene sulphinic acid; 2. p-acetamido benzene sulphonic acid; 3. p-amino benzene sulphinic acid; 4. p-amino benzene sulphonic acid; 5. p-amino thiophenol.

The product distribution varies depending upon the condition. Table I shows the amount of different reduction product formed while adopting different electrolytic conditions. When the zinc deposited copper electrode is used fairly good yield of the reduction products were obtained and product distribution ratio between the two major

TABLE I: Electrolysis of p-acetamido benzene sulphonyl chloride under various conditions

Electrode	Electrolyte	C D A/dm^2	Temp K	C E (%)	Y E (%)	Main reduction product
Copper/lead	aq.HCl/H_2SO_4	2.0	303 ± 2	-----	25-30	Thiophenol
Copper/lead	aq.HCl/H_2SO_4	2.0	313 ± 2	-----	10-15	Thiophenol
Copper/lead	aq.HCl/H_2SO_4	1.5	293 ± 2	50	50-55	Thiophenol
Copper/lead	aq.HCl/H_2SO_4	1.5	308 ± 2	50	50-55	Thiophenol
Copper/lead	aq. NaCl	2.0	298 ± 2	65	65-70	P-acetamido sulphinic acid & thiophenol
Znc deposited copper	aq. NaCl	2.0	298 ± 2	70	70-75	P-acetamido sulphinic acid and thiophenol

products namely p-amino benzene sulphinic acid and p-acetamido benzene sulphinic acid in 3:4.5. The reduction mechanism while using zinc deposited copper electrode differs from that when plain copper or lead electrodes are used. While using the copper or lead as the cathodes the electron transfer takes place directly to the organic species. But in the zinc mediated reduction the reduction proceeds viz. zinc deposition and dissolution can be represented as follows:

$$2RSO_2Cl + Zn \longrightarrow (RSO_2)_2Zn$$

$$(RSO_2)_2Zn + HCl \longrightarrow 2RSO_2H + ZnCl_2$$

$$Zn^{2+} + 2e \longrightarrow Zn$$

CONCLUSION

The reduction of p-acetamido benzene sulphonyl chloride is reduced in acidic condition both in alcoholic or aqueous medium to thiophenol with some amount of hydrolysed product formation using Zn as mediator one can prepare sulphinic acid along with some hydrolysed product.

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